Homework # 7: 2, 3a, 5, 6, 7, 9

2) *a.* What is the vapor pressure of pyrene above a saturated solution of pyrene in water?

Solution:

Don't confuse the issue here. For any problem like this, determine what the system is, and then write out the chemical potentials. In this instance, the easiest thing to do is draw a picture(see 1). Since the solution is saturated, it's like having a large bar of solid pyrene in water. Now, since we're at
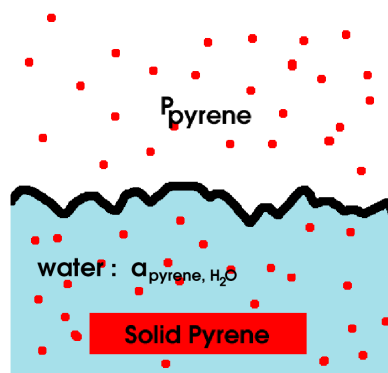

Figure 1: water-solid-vapor Equilibrium

equilibrium, we can make a statement about the chemical potentials:

$\mu_{pyrene,\,solid} = \mu_{pyrene,\,H_2O} = \mu_{pyrene,\,vapor}$.

We can cut out the middle man (the pyrene in solution) and just say that we have an equilibrium established between solid pyrene and pyrene vapor. For this particular equilibrium, we have been told that the vapor pressure of pyrene will be P_1, and that's the answer.

b. What if you had another layer of ethanol?

Solution:

So we'll do the same thing as before: draw a picture and determine chemical potentials. The only change in our picture (see 2) is that instead of having a water layer, we have a mixed water-ethanol layer:

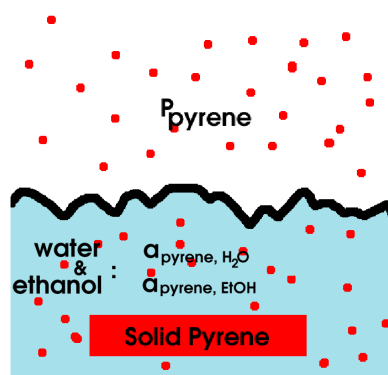Our statement about chemical potentials is as follows:

Figure 2: Water-ethanol/solid/vapor equilibrium

$\mu_{pyrene,\,solid} = \mu_{pyrene,\,H_2O} = \mu_{pyrene,\,ethanol} = \mu_{pyrene,\,vapor}$. Again, you can ignore the pyrene in water and ethanol, and just equate the solid and the vapor. The answer is P_1 again.

Note that for both parts a and b, if the solution weren't saturated, we couldn't say that $\mu_{pyrene,\,solid} = \mu_{pyrene,\,H_2O}$. Then we would have to use Henry's Law.

$c.$ Find K when you add it to 0.1 M cytosine solution
Solution:
For the reaction
$$P(solution) + C(solution) \rightleftharpoons P \cdot C(solution)$$
We know that $K = \frac{P \cdot C(solution)}{P(solution)C(solution)}$. So we only need to evaluate those concentrations in order to find K.

Since the increase in solubility is entirely due to the complexation, this means that the amount of $P \cdot C(solution)$ is the difference between the new solubility and the old solubility. Therefore:

$$
\begin{aligned}
P \cdot C(solution) &= \text{old solubility} - \text{new solubility} \\
&= 1.1 \times 10^{-3}M - 1.0 \times 10^{-4}M \\
&= 1 \times 10^{-3}M
\end{aligned}
$$

The amount of cytosine in solution is just (total amount - amount in complex), so:
$C(solution) = 0.10M - 1 \times 10^{-3}M = 9.9 \times 10^{-2}M$.

Finally, $P(solution)$ is just the amount of pyrene which dissolves normally in water, which is just the solubility of $1 \times 10^{-4}M$.
Then $K = \frac{1 \times 10^{-3}}{(9.9 \times 10^{-2})(1 \times 10^{-4})} = 101$.
Now, they also ask for K for a slightly different reaction:

$$P(solid) + C(solution) \rightleftharpoons P \cdot C(solution)$$

The amount of cytosine and the pyrene-cytosine complex will remain unchanged (since it's essentially the same reaction); however, the activity of $P(solid)$ is different than the activity of $P(solution)$. In this case, since the solid is a pure substance, than $P(solid) = 1$. This gives $K = \frac{1 \times 10^{-3}}{(9.9 \times 10^{-2})(1)} = 0.0101$.

3) $a.$ What form of CH_4 has the lowest standard chemical potential?
Solution:
Remember, chemical potential tells you how stable (or how reactive) a substance would be. If chemical potential is high, it says your substance is very unstable, and likely to move to a different form. The lower the chemical potential, the more stable it is. So this question can be rephrased as follows: "Which form of CH_4 is most stable at 298 K and 1 atm of pressure?" Or in other words, in what form would you expect to find methane? The answer is that methane is a gas at STP; therefore, $CH_4(g)$ has the lowest chemical potential.
Now, you might be saying to yourself, "How was I supposed to know that methane was a gas at STP? What if I hadn't know that?" Limited perusal of the book indicates that if you had not, in fact, known that methane is normally found as a gas, you would not have been able to answer this problem.

5) $a.$ What's the chemical potential required to synthesize ATP inside the mitochondria?
Solution:
For the reaction

$$ADP + Pi \rightarrow ATP + H_2O \qquad\qquad \Delta G^\circ = 31.0 \; kJ/mol \text{ (from pg. 167)}$$

we know that

$$\Delta\mu = \Delta G \;\; = \;\; \Delta G^\circ + RT \ln Q$$

$$= \quad 31.0 \ kJ/mol + (8.314 \ J/mol \, K)(298K) \ln \left(\frac{1 \times 10^{-3}}{(1 \times 10^{-3})(2.5 \times 10^{-3})} \right)$$

$$= \quad 45.8 \ kJ/mol$$

P.S. Who really believes that the temperature of your mitochondria is 298 K?

b. What's the free energy for moving a mole of protons from the outside to the inside?
Solution:
There are two parts to this free energy. First, we have a part which comes from moving a proton from a low concentration of H+ (pH 7.0) to a higher concentration (pH 7.0 - ΔpH = pH 5.5). Secondly, we have a part which comes from moving a charged particle across an electric potential. Therefore, we can write:

$$\begin{aligned} \Delta G \quad &= \quad \Delta G(pH \, gradient) + \Delta G(potential) \\ &= \quad RT \ \ln \left(\frac{a_{H+, \ inside}}{a_{H+ \ outside}} \right) - nF\varepsilon^\circ \\ &= \quad (8.314 \ J/mol \, K)(298K) \ln(10^{-1.5}) - (-1 mol \ e^-)(96,500 \ C/mol \, e^-)(-140 \times 10^{-3} \ V) \\ &= \quad -8.56 \ kJ/mol - 13.51 \ kJ/mol \\ &= \quad -22.1 \ kJ/mol \end{aligned}$$

Note that since we are transfering 1 proton, this has minus the charge of one electron, so we use n=-1. Since we need 45.8 kJ for one mole of ATP, one mole of H+ does not provide enough energy.

c. How many H+ do you need to transfer to create one mole of ATP?
Solution:
Assuming the process is 100 % efficient (which it isn't), then if you need 45.8 kJ/mol to hydrolize ATP, and you can get 22.1 kJ/mol by transfering protons, then you'd need $\frac{45.8}{22.1} = 2.07$ protons transferred per ATP. So you need more than 2.

6) *a.* Write the expression for the change in chemical potential for
1 mol NaCl (0.05 M, inside) $\rightleftharpoons$ 1 mol NaCl (0.20 M outside)
Solution:
Since $\mu = \mu^\circ + RT \ln(a)$, we can write the chemical potential for the inside and the outside as follows:
$\mu_{inside} = \mu^\circ + RT \ln(a_{inside})$
and $\mu_{outside} = \mu^\circ + RT \ln(a_{outside})$
Subtracting the two, we get
$\Delta\mu = RT \ln(a_{outside}/a_{inside})$, where $a_{outside}$ is the activity of NaCl outside the membrane and a_{inside} is the activity of NaCl inside the membrane.

b. Determine $\Delta\mu$.
Solution:
We have an expression for $\Delta\mu$ from part a. If we assume the NaCl acts ideally, the activity is just the concentration, and

$$\begin{aligned} \Delta\mu \quad &= \quad RT \ln(\frac{a_{outside}}{a_{inside}}) \\ &= \quad (8.314 \ J/mol \, K)(298K) \ln(\frac{0.20 \ M}{0.05 M}) \end{aligned}$$

$$= \quad 3.43 \ kJ/mol$$

So the reaction is not spontaneous.

c. What if it happens for three moles?
Solution:
You multiply the number above by three moles:
$\Delta\mu = \frac{3.43kJ}{mol} \times 3mol = 10.29kJ$

d. What if the activity inside is the same as the activity outside?
Solution:
Than $a_{outside}/a_{inside} = 1$, so $\ln(a_{outside}/a_{inside}) = 0$, and $\Delta\mu = 0$.

e. What if it happens at equilibrium?
Solution:
At equilibrium, $\Delta G = \Delta\mu = 0$.

f. For ATP hydrolysis, if the ATP:ADP ratio is 10:1, determine how much phosphate you must have if $\Delta G = -40 \ kJ/mol$.
Solution:
We know that $\Delta G = \Delta G^\circ + RT \ln Q$. We have both ΔG and ΔG°; we have everything we need for Q but the phosphate concentration. So we'll solve for that:

$$
\begin{aligned}
\Delta G &= \Delta G^\circ + RT \ln Q \\
-40 \ kJ/mol &= -31.7 \ kJ/mol + (8.314 \ J/molK)(310 \ K) \ln\left(\frac{[P_i]}{10}\right) \\
\frac{-8.3 \times 10^3 \ J/mol}{8.314 \ J/mol \times 310} &= -\ln(10) + ln[P_i] \\
-3.22 &= -2.302 + \ln[P_i] \\
-.917 &= \ln([P_i]) \\
P_i &= e^{-.917} \\
&= .39M
\end{aligned}
$$

g. How much phosphate must you have if you're at equilibrium?
Solution:
At equilibrium, $\Delta G = 0$ so we set this up exactly as before:

$$
\begin{aligned}
\Delta G &= \Delta G^\circ + RT \ln Q \\
0 \ kJ/mol &= -31.7 \ kJ/mol + (8.314 \ J/molK)(310 \ K) \ln\left(\frac{[P_i]}{10}\right) \\
\frac{31.7 \times \ 10^3 J/mol}{8.314 \ J/mol \times 310} &= -\ln(10) + ln[P_i] \\
14.6 &= ln[P_i] \\
P_i &= e^{14.6} \\
&= 2.19 \times 10^6 \ M
\end{aligned}
$$

This number is gigantic; since pure water is only 56 M, you can pretty easily guess that this concentration of phosphate is flat-out impossible. There are two conclusions you could make. You could conclude that it's impossible for this reaction to reach equilibrium. But this isn't the case. What *is* true is that it is impossible to reach equilibrium if the ATP:ADP ratio is maintained at 10:1–in other words, this reaction could reach equilibrium, but only if ADP significantly outnumbered ATP.

7 Draw a Scatcherd plot and determine K and N.
 Solution:
For a Scatcherd Plot, you need to plot ν versus ν / [A], where ν is the amount of ligand bound to each macromolecule, and [A] is the amount of ligand which is free in solution. In particular, [A] is the amount of ligand which exists on the side of the dialysis membrane without macromolecules, and ν = total amount of stuff on side with macromolecules - total amount of stuff on side without macromolecules, all divided by the total concentration of the macromolecule.
By repetitive adding and dividing, we can determine the following values:

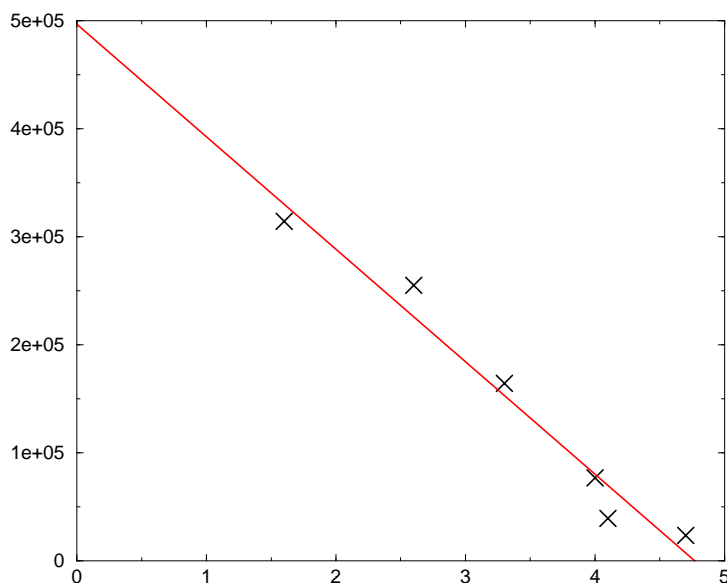| [A]	ν	$\frac{\nu}{[A]}$
0.51×10^{-5}	1.6	3.14×10^5
1.02×10^{-5}	2.6	2.55×10^5
2.01×10^{-5}	3.3	1.64×10^5
5.22×10^{-5}	4.0	7.66×10^4
10.50×10^{-5}	4.1	3.90×10^4
20.00×10^{-5}	4.7	2.35×10^4

We graph this:

Figure 3: Scatcherd Plot for 7)

 The red line indicates a linear regression which was done on the data, which found that
y=-1.04 $\times 10^5$ x + 4.96 $\times 10^5$
This gives us that K= 1.04 $\times 10^5$, and the intercept of the line, $4.96 \times 10^5 = NK$. Dividing by K gives us the number of binding sites is 4.71; this rounds to 5 binding sites.

9 *a*. Calculate K.
Solution:
The first thing we should do is determine the number of molecules we have. In order to figure this out, we need to use the osmotic pressure:

amount of enzyme $= \frac{\pi}{RT} = \frac{2.4 \times 10^{-3} \ atm}{(0.08206 \ L \ atm/mol \ K)(293 \ K)} = 9.98 \times 10^{-5} M$.

Since $\frac{\nu}{[A]} = K(N - \nu)$ we can rearrange and find that $K = \frac{\nu}{[A]} \frac{1}{N - \nu}$.

Using the information provided,

$$
\begin{aligned}
\nu &= \frac{\text{amount of ATP inside the bag} - \text{amount of free ATP outside}}{\text{total amount of enzyme}} \\
&= \frac{3.0 \times 10^{-4} M - 1.0 \times 10^{-4} M}{9.98 \times 10^{-5} M} \\
&= 2.00
\end{aligned}
$$

[A] is just the amount of free ATP, which is $1.0 \times 10^{-4} M$.

N is the number of binding sites per molecule, which is 4. Plugging these results in to the above equation for K gives us:

$$
\begin{aligned}
K &= \frac{\nu}{[A]} \frac{1}{N - \nu} \\
&= \frac{2.0 \times 10^{-4}}{1.0 \times 10^{-4}} \frac{1}{4 - 2.00} \\
&= \frac{2 \times 10^{-4}}{2} \\
&= 1.0 \times 10^{-4}
\end{aligned}
$$

b. Calculate ΔH and ΔS.

Solution:

The y-intercept of the scatcherd plot is NK. So for 20 C, the y intercept is 4 and for 37 C the y-intercept is 2. Therefore, $\frac{K_{20}}{K_{37}} = \frac{4}{2}$. Using equations gleaned from chapter 4, we get:

$$
\begin{aligned}
\ln\left(\frac{K_{37}}{K_{20}}\right) &= -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\
\Delta H &= -\frac{R \ln(K_{37}/K_{20})}{1/T_2 - 1/T_2} \\
&= -\frac{8.314 \ J/mol \ K \ln(1/2)}{1/310 \ K - 1/293 \ K} \\
&= 30.8 \ kJ/mol
\end{aligned}
$$

To find ΔS, we need only find a value for ΔG and then plug in our ΔH value. In particular, $\Delta G(20) = -RT \ln K = -8.314 \ J/mol K \times 293 K \ln(10^4) = -22.4 \ kJ/mol$

Then, $\Delta S = \frac{\Delta H - \Delta G(20)}{293 K} = 181 \ J/K$.